Electrochemical Performances of Gel Polymer Electrolytes with PMMA -IPNs

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Introduction

A gel-type polymer electrolyte has been suggested in lithium-ion polymer battery. When an acrylate or a methacrylate monomer was used in a gel polymer electrolyte, the precursor can be easily infiltrated into the electrodes because it has relatively low viscosity. The resulting polymer network has high mechanical properties. A IPN system can be formed by the simultaneous formation of the two networks or by sequential formation, with one network formed first and a monomer then added and, subsequently, polymerized and cross-linked.

In this study, precursor for the GPE was prepared using polymethyl methacrylate-methyl methacrylate IPN system as a reactive material, benzoyl peroxide (BPO) as a thermal initiator. The $LiCoO_2$/GPE/graphite cells are prepared and their electrochemical properties were evaluated at various current densities and temperatures.

Experimental

PMMA IPN system was prepared by dropping methylmethacrylate (MMA) into PMMA at 60 ^oC in oxygen atmosphere. Hexanediol dimethacrylate (HDDA) was used as a cross-linker. Battery grade solution of 1.0 M $LiPF_6$/EC:DEC (1:1 vol%) was obtained from Cheil Industries. BPO [Aldrich Chemical Co.] was used as an initiator. A precursor containing of 95 vol% electrolyte and 5 vol% curable mixture was polymerized by a thermal reaction at 80 ^oC for 40 minutes. The viscosity was measured by means of a viscometer DV-II$^+$ (Brookfiel Co.). The ionic conductivity of GPE was measured using an AC impedance analyzer (IM6, Zahner Elektrik) with a stainless steel blocking electrode cell.

Lithium cobalt oxide electrodes were prepared by mixing 93wt% $LiCoO_2$ (Osaka Gas) with 4 wt% super P black and 3 wt% PVdF, and then coating the mixture on an aluminum foil. Graphite electrode were prepared with 95 wt% MCF(milled carbon fiber) and 5 wt% PVdF. Celgard 2500 was used as a separator. The electrodes were stacked and inserted into an aluminum-laminated film. The assembled cells were polymerized in an oven.

The charge and discharge cycling tests were conducted galvanostatically with a Toyo battery test system (TOSCAT-3100K). The discharge curves were obtained at different current rates to obtain the rate capabilities of the cells and also at various temperatures.

Results and discussion

The electrolyte of the cell should also allow low-temperature performances, because the commercial batteries are sometimes used in these conditions. It is especially pointed out that performance of lithium-ion polymer batteries at low temperature and high current is low compared with lithium-ion batteries having the liquid electrolyte. The ionic conductivity of a gel polymer electrolyte containing 5 vol. % reactive-material obtained at various temperatures is shown in Figure 1. The ionic conductivity of GPE at 20 ^oC is around 5.8 x 10^{-3} $S\cdot cm^{-1}$ and it is quite high, i.e. 1.4 x 10^{-3} $S\cdot cm^{-1}$, even at –20 ^oC.

Cyclic voltammograms for the gel polymer electrolyte on the stainless steel electrodes are measured up to ca. 5.2 V versus Li/Li^+. No peaks were observed up to 4.8 V. There is no problem with the electrochemical stability, because charging voltage for lithium-ion battery using lithium cobalt oxide is about 4.2 V.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using the gel polymer electrolyte, a $LiCoO_2$/GPE/graphite cell was fabricated. The rate capability of the $LiCoO_2$/GPE/graphite cell was evaluated. The discharge curves obtained at different current rates are given in Figure 2. The cell delivered a discharge capacity of 448 mAh at current density of 0.5 $mA\cdot cm^{-2}$. The discharge capacity slowly decreased with current rate, which was due to polarization. A useful capacity of 438 mAh is obtained at current density of 1.1 $mA\cdot cm^{-2}$ (0.5C rate), which is 98% of the discharge capacity at 0.2C rate. The capacity of 366 mAh is available even at the 1.0C rate, which is 82% of the discharge capacity at 0.2C rate.

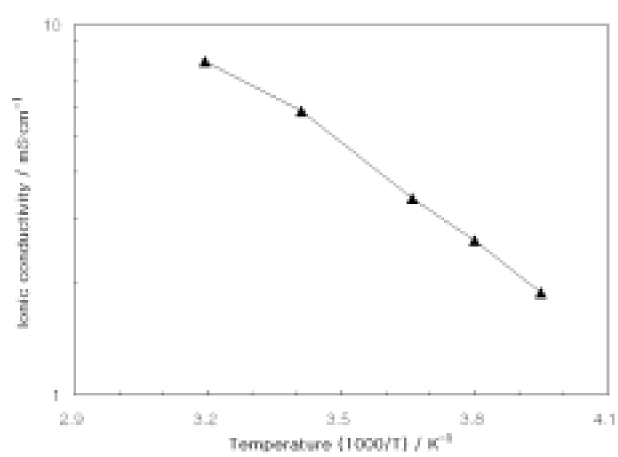

Fig. 1 Ionic conductivity of the gel polymer electrolyte at various temperatures.

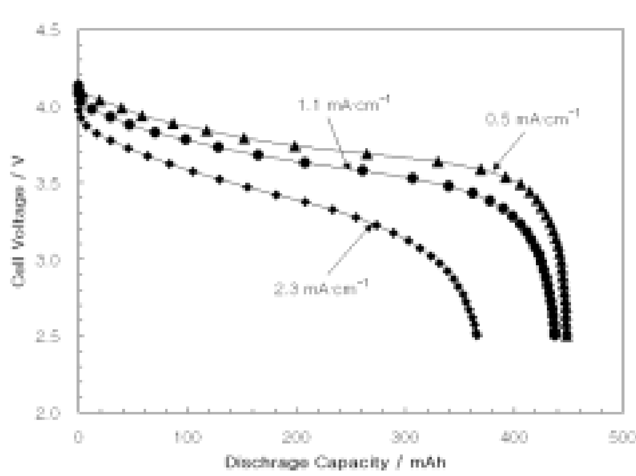

Fig. 2 Typical discharge curves for $LiCoO_2$/GPE/graphite cell at various current densities at 20℃.